

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Active Porous Alumina of High Mechanical Strength

We, PRODUITS CHIMIQUES PECHINEY-SAINT-GOBAIN, a body corporate organised and existing under the laws of France, of 16, Avenue Maignon, Paris 8e, France, do hereby
5 declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention is concerned with catalyst carriers in the form of active porous alumina of high mechanical strength.

Heterogeneous catalysis of certain reactions sometimes necessitates the use of such carriers, having active surfaces of the order of some
15 square metres or at the most of the order of some tens of square metres per gram and a considerable porosity in pores of some hundreds of Angstrom units. It is difficult to
20 give such an active surface to carriers obtained from large-surfaced active alumina without detracting excessively from the mechanical strength of the alumina. So although calcination of active alumina at a fairly high temperature has a good effect on microporosity and
25 thus on the specific surface, and although microporosity then evolves into macroporosity which is necessarily one of the features of the alumina to be used as a carrier in the heterogeneous catalysis of certain reactions, the mechanical strength is greatly reduced as a result of the calcination temperatures of the order of 850°C, which in any case leave the active surface areas too great in view of the reactions
30 to be catalysed.

In accordance with the present invention, such alumina catalyst carriers of high mechanical strength are obtained by bringing granulates or conglomerates of active alumina having a specific surface area of at least .200
40 sq.m./g. in an autoclave in the presence of water, to a temperature of over 100°C and preferably from 150 to 250°C for a time ranging preferably from 1 to 8 hours and calcining them at a temperature of at least 500°C.

[Pm]

The invention also concerns the granulates or conglomerates of alumina obtained by this method.

The method according to the invention avoids the drawbacks noted above and makes
50 it possible to obtain carriers having small specific surfaces which vary from a few square metres to some tens of square metres per gram preferably less than 80 square metres per gram without thereby sacrificing the mechanical
55 strength of the carriers, which is maintained throughout long use.

Autoclave treatment of large-surfaced active alumina generally speaking increases the macroporosity of the alumina after calcination at a relatively low temperature, while at higher temperature the macroporosity is only slightly increased. On the whole, the microporosity of alumina that has been treated in an autoclave and calcined is somewhat lower than that of
60 alumina not so treated at the same temperature.

In the following illustrative Examples, which are given to show the effect of the autoclave treatment on the strength of small-surfaced alumina pellets, the figures given for the microporous volumes (pores less than 0.1μ in diameter) and for the macroporous volumes (pores greater than 0.1μ in diameter) are intended strictly as an indication in order to show the general trend of the variations in the characteristic sizes of the pellets; but obviously the distinction between the microporous volume responsible for the active surface and the macroporous volume is a somewhat conventional one and cannot give any true picture of the distribution of pore sizes whereas the active surfaces, which are measured directly, are sizes which one must know in order to use such catalyst carriers.
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EXAMPLE 1

From a batch No. 1 of alumina pellets 2 to 5 mm. in diameter made by impregnating with water and conglomerating in a tableting "machine," a series of samples are taken and
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calined at temperatures ranging from 500 to 1600°C. Another series of samples is taken from the same batch and, before being calined at the same temperatures, is treated in an autoclave in the presence of water at 210°C for 4 hours. For each of the various samples the specific surface, microporous volume (pores less than 0.1 μ in diameter), macroporous volume (pores greater than 0.1 μ in diameter and resistance to crushing are measured. The results are set out in Table 1 below.

TABLE 1

Calci- nation tempe- rature °C.	Pellets from Batch 1 not Treated in Autoclave			Pellets from Batch 1 Treated in Autoclave				
	Active Surface m ² /g.	Micro- porous volume cc/100 g.	Macro- porous volume cc/100g.	Resist- ance to crushing kg.	Active surface m ² /g.	Micro- porous volume cc/100 g.	Macro- porous volume cc/100 g.	Resist- ance to crushing kg.
500	379	50	17	11	95	40	32	4.4
800	163	53	21	8	65	41	33	5.3
1000	127	48	19	7	45	39	35	4
1200	9	8	52	2	20	30	30	9
1400	1.23	0.2	30	9	3	0.5	48	9
1600	0.23	0.1	23	10	2	0.3	44	15

The effect of the autoclave treatment on the pellets of high macroporosity is marked. Very high macroporous volumes are obtained for surfaces smaller than with untreated pellets, and there is an acceptable degree of mechanical resistance.

EXAMPLE 2

From a different lot (Batch No. 2) of alumina pellets 2 to 5 mm. in diameter, also made

by impregnating active alumina with water and conglomerating it in a tableting machine, two series of samples are taken as in the preceding example, one acting as a control and the other being treated in an autoclave in the presence of water for four hours at 210°C. The various calcination temperatures range from 650 to 1600°C. The same sizes are measured as in the previous example. The results are set out in table 2 below.

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TABLE 2

Calci- nation Tempera- ture °C.	Pellets from Batch 2 Not treated in Autoclave				Pellets from Batch 2 treated in Autoclave			
	Active Surface m ² /g.	Micro- porous volume cc./100g.	Macro- porous volume cc./100g.	Resist- ance to crushing kg.	Active surface m ² /g.	Micro- porous volume cc./100g.	Macro- porous volume cc./100g.	Resist- ance to crushing kg.
650	212	39	6	11.4	73	25	25	10
950	146	40	6	11.6	48	26	23	11
1100	41	30	13	3.6	26	22	27	10
1200	17	24	19	4	8	13	27	13
1400	6.7	11	30	3	2	3.5	24	20
1600	2.3	2.8	25	10	1.6	0.6	21	25

The effect of autoclave treatment is very clear in this case, it is possible to obtain pellets of various specific surfaces and of high strength, whereas untreated pellets are much less strong when the surfaces are small, even with porous volumes of the same order.

WHAT WE CLAIM IS:—

1. The method that comprises heating granulates or conglomerates of active alumina having a specific surface are of at least 200 sq.m./g at a temperature exceeding 100°C. in

an autoclave in the presence of water, and then calcining them at a temperature of at least 500°C to produce catalyst carriers of high mechanical strength in the form of porous active alumina.

2. A method as claimed in claim 1, in which the temperature of the autoclave is from 150 to 250°C.

3. A method as claimed in claim 1 or 2, in which the duration of treatment in the autoclave is from 1 to 8 hours.

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4. A method as claimed in claim 3, in which the said duration is about 4 hours.
5. A method as claimed in claim 1, substantially as hereinbefore described with reference to either of the foregoing Examples.
6. Catalyst carriers of porous active alumina obtained by a method as claimed in any preceding claim.
7. Catalyst carriers as claimed in claim 6, having an active surface smaller than 80 square metres per gram. 10

For the Applicants,
D. YOUNG & CO.
Chartered Patent Agents,
9, Staple Inn,
London, W.C.1.

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